

UK Patent Application (19) GB (11) 2 331 942 A

(43) Date of A Publication 09.06.1999

(21) Application No 9826851.9

(22) Date of Filing 08.12.1998

(30) Priority Data

(31) 9725898

(32) 08.12.1997

(33) GB

(71) Applicant(s)

Albright & Wilson UK Limited
(Incorporated in the United Kingdom)
P O Box 3, 210-222 Hagley Road West, Oldbury,
WARLEY, West Midlands, B68 0NN, United Kingdom

(72) Inventor(s)

Adrian Charles Archer
Roger James Putman
Susan Marie Rush

(74) Agent and/or Address for Service

Barker Brettell
138 Hagley Road, Edgbaston, BIRMINGHAM,
B18 9PW, United Kingdom

(51) INT CL⁶

C23F 11/167, B05D 7/14, C23C 22/00

(52) UK CL (Edition Q)

B2E EAM E1202 E1307 E1310 E409S E459T

(56) Documents Cited

GB 2322627 A	GB 2309972 A	GB 2121419 A
GB 1489241 A	GB 1261554 A	EP 0846733 A
EP 0780406 A	WO 92/12806 A	US 4978399 A

(58) Field of Search

UK CL (Edition Q) B2E EACA EACB EAH EAK EAM
EANA EANC EKB
Online (WPI); Selected UK specifications

(54) Abstract Title

Treating metal surfaces

(57) A composition comprising at least one organo phosphonate or organo phosphonate species used for the treatment of a variety of metal surfaces to inhibit corrosion and improve adherence of coatings. The composition can include a homopolymer or copolymer of an organo phosphonate or organo phosphonate species such as vinylphosphonic acid, vinylidene-1, 1-diphosphonic acid or phenyl vinyl phosphonic acid. The composition is applied to the metal surface in a controlled amount to optimise performance and to reduce waste.

GB 2 331 942 A

PROCESS FOR TREATING METAL SURFACES

The present invention relates to a composition for treating surfaces of a variety of metals to inhibit corrosion and improve adherence of 5 coatings to the surface, and to a process for treating surfaces with the composition and to a metal surface treated by such a process.

Metal surfaces are prone to corrosion, which weakens the strength of the metal over a period of time. There are many products available 10 which help prevent the corrosion of metals. In many cases, however, the product is specific for one metal and therefore must be changed with the metal, which can lead to waste and cross-contamination.

Many known coating processes contain chromium compounds, 15 however there is increasing pressure to remove chromium compounds from metal pretreatments. There are a number of known chromium free processes. However these processes are generally complicated and require the use of catalysts and accelerators to speed up the coating process. The catalysts and accelerators may also need to be varied 20 according to the metal surface.

Subsequent to treatment with a corrosion inhibitor, the metal surface often has one or more further coatings (e.g. paint) applied thereto and accordingly the corrosion inhibitor should permit or promote good 25 adhesion of such further coatings.

Accordingly the present invention provides a composition adapted to treat the surface of more than one type of metal, the composition comprising at least one organo phosphonate or organo phosphonate 30 species.

Preferably the organo phosphonate or organophosphonate species is a polymer.

5 Preferably, the phosphonate species included in the composition of the present invention is a mono- or di-phosphonic acid, ester or salt.

Preferably, the phosphonate species is a mono - or di-phosphonic acid, ester or salt containing one or more carbon-to-carbon bonds.

10 For example, the phosphonic acid may be an alkyl, aryl or alkenyl phosphonic acid such as octyl phosphonic acid, phosphonosuccinic acid, phosphonopropanoic acid, vinylphosphonic acid (VPA), vinylidene-1, 1-diphosphonic acid (VDPA) or phenyl VPA.

15 The composition may contain a polymer with pendant phosphonic or di-phosphonic acid groups.

20 Thus, the composition may comprise a homopolymer of a phosphonic acid such as vinylphosphonic acid (VPA), vinylidene-1,1-diphosphonic acid (VDPA), phenyl VPA, or a salt or an ester of any of the said acids.

25 Alternatively, the composition may comprise a copolymer of a phosphonic acid (or a salt or an ester of said acid) together with a second co-monomer.

30 The second co-monomer may be an unsaturated carboxylic acid, such as acrylic acid, maleic acid or methacrylic acid (or salts or esters of any of the said acids).

The second co-monomer may alternatively be an unsaturated sulphonic acid, such as vinylsulphonic acid (VSA), or acrylamido methyl propane sulphonic acid (AMPS), (or an ester or a salt of any of the said acids).

5

The second co-monomer may be any other unsaturated compound (such as acrylonitrile) which is co-polymerisable with the phosphonic acid.

10

Finally, the composition may comprise a terpolymer of an unsaturated phosphonate species and other suitable comonomers such as an unsaturated sulphonic acid, an unsaturated carboxylic acid or acrylamide.

15

For example, the composition may comprise a terpolymer of VPA, VSA and acrylic acid.

Alternatively the composition may contain a polyester containing pendant phosphonic acid groups.

20

Where the composition is a copolymer of vinyl phosphonic acid (VPA) with acrylic acid (AA) the ratio of the components is preferably between 1:99 and 99:1 (VPA:AA). Most preferably, the ratio is between 2:98 and 30:70 (VPA:AA).

25

The nature of the composition allows adherence of the composition to a number of metal surfaces such as cold rolled steel, electro galvanised steel, hot dip galvanised steel and related alloyed alternatives such as Galfon (Registered Trade Mark) or Zalutite (Registered Trade Mark), 30 stainless steel, tin plate or terne plate (lead coated steel).

The metal surface will not be aluminium or aluminium alloy surfaces.

5 The nature of the composition avoids the need for a catalyst or an accelerator as adherence of the composition to a metal surface occurs quickly.

10 Although it is not intended that the present invention be construed with respect to any particular theory, it is believed that the composition of the present invention adheres to metal surfaces by means of one or more 15 of a number of possible methods which include:-

1) An interaction rather than a chemical reaction occurring between the composition and the metal surface;

15

2) An acid-base reaction occurring between the composition and the metal surface;

20

3) The formation of a metal phosphonate salt which forms a coating on the metal surface.

25

The present invention further provides a process for treating a metal surface, the process including the steps of contacting said surface with a controlled amount of a composition according to the present invention dissolved in a solvent and removing the solvent.

In one embodiment of the present invention the amount of composition to be applied to the metal surface may be controlled by dilution of the composition and adjustment of the wet film thickness.

30

Preferably the amount of composition residue left on the surface after drying is in the range of $0.001\text{g}/\text{m}^2$ to $10.000\text{g}/\text{m}^2$, more preferably $0.005\text{g}/\text{m}^2$ to $5.000\text{g}/\text{m}^2$ and most preferably 0.01 - $1.00\text{g}/\text{m}^2$

5 The composition may be applied to the metal surface by flood-spraying or immersion, the wet film being preferably metered to the required thickness (for example by means of one or more sets of squeegee rollers). The excess composition may be recovered and reused. Alternatively, the composition may be applied by roller-coating onto the
10 metal surface. Roller-coating gives a more uniform coating than flood-spraying followed by squeegeeing and avoids waste of the composition.

In a second embodiment of the present invention the amount of composition to be applied to the metal surface may be controlled by a
15 reaction occurring between the metal surface and the composition.

Preferably the surface is immersed in the composition, or an aqueous solution thereof, preferably for 0.5 seconds to five minutes and preferably at a temperature of 5 - 100°C .

20 The metal surface may be wiped or rinsed after contact with the composition. Wiping or rinsing the metal surface after contact with the composition will remove any unbound composition.

25 A reaction between the metal surface and the composition may also occur in the first embodiment of the invention but the amount of composition is controlled in this case by the metering of the wet film thickness.

30 The composition is preferably applied as an aqueous solution.

After application to the metal surface, the solvent may be removed by allowing the composition to dry passively at ambient temperature. Alternatively, the composition may be dried positively at a temperature of 5 60-200°C for 0.1-10 minutes more preferably 80-180°C for 0.1-5 minutes and most preferably 140-180°C for 0.5-2 minutes.

The process is applicable to metal surfaces such as cold rolled steel, electro galvanised steel hot dip galvanised steel, and related alloyed 10 alternatives such as Galfon (Registered Trade Mark) or Zalutite, (Registered Trade Mark) stainless steel, tin plate or terne plate (lead coated steel).

The process is not applicable to aluminium or aluminium alloy 15 surfaces.

The metal surface to which the composition is to be applied may be cleaned, for example by treatment with an aqueous acid or alkaline degreasing preparation and brushing.

20

The metal surface to which the composition has been applied may be wiped or rinsed.

The advantages of these methods of application of the composition 25 include the uniform application of the composition to the metal surface, the low capital cost and the possibility of recycling the excess composition to avoid waste.

The present invention further provides a metal surface treated by 30 the process described in the immediately-preceding paragraphs.

The invention will now be illustrated by way of the following examples:-

5 **General example of method of applying the composition**

The metal surface to which the composition containing at least one phosphate species is to be applied is cleaned by alkaline cleaning, and brushing if necessary, to remove grease, dirt and chemical films.

10

The metal surface is then rinsed with water, any excess being removed by means of squeegee rollers. The final rinse water is hot to aid drying of the rinsed metal surface.

15

The composition is applied to the metal surface in a controlled amount to achieve a thin coat and to avoid waste. The method of applying a controlled amount of coating can be any one of the methods described in the description and examples.

20

The metal surface coated in the composition is allowed to dry at ambient or elevated temperature before any further coatings, such as paint, are applied.

25

EXAMPLES

The tests used in the following four examples are known standard tests performed according to the following British standards:-

30

Impact, falling weight	BS3900:E3:1966
Bend Test	BS3900:E1
Cupping Test	BS3900:E4:1995
Cross Cut Test	BS3900:E6:1992
Neutral salt spray	ASTM B117-90
Evaluation of results	BS3900:H2:1983

Example 1 - Adhesion Performance of Further Coatings with Surfaces

5 Treated with the Composition of the Present Invention

A polymer containing 30 mol% VPA and 70 mol% AA was applied to 3 panels of different metals at two concentrations using the following method.

10

The panels were cleaned in Ridoline (Registered Trade Mark) 1089 (15g l⁻¹) at 60°C for 15 seconds, rinsed in mains water, rinsed in deionised water and dried.

15

The polymer solutions were applied at 1%w/w and 10%w/w in deionised water on a sheen spinner for 20 seconds and stoved at 160°C for 1 minute.

20

The panels pre-treated in this way were coated with a Beckers Epoxy stoving primer. The primer was applied using a 25μm bar coater, stoved at 250°C for 2 minutes 10 seconds (PMT (Peak Metal Temperature) 214-224°C), and given a cold water quench.

The adhesion results are shown in Table 1 below.

Table 1 - Adhesion Testing of Pretreated Panels

	Cross Cut		Falling Impact ^(a)	Cupping Test (6mm) ^(a)	Bend Test (3T) ^(a)
	dry	wet			
1% on Zalutite	0	0	0	0	0
1% on HDG	0	0	0	0	0
1% on Galfan	0	0	0	5	0
10% on Zalutite	0	1	0	0	0
10% on HDG	0	1	0	50	20
10% on Galfan	0	0	0	25	0
HDG control ^(b)	0	1	35	N/A	100

5

legend:- (a)% coating removed; (b) unpretreated HDG (Registered Trade Mark)

10 Example 2 - Adhesion Performance of Further Coating with Surfaces Treated with the Composition of the Present Invention

A polymer containing 30mol% VPA and 70mol% AA was applied to 3 panels of different metals at two concentrations using the following method;

15

The panels were cleaned in Ridoline 1089 (15 g l⁻¹) at 60°C for 15 seconds, rinsed in mains water, rinsed in deionised water and dried.

20 The polymer solutions were applied at 1%w/w and 10%w/w in deionised water by immersing the panels in the working solution for

1 minute at 50°C, rinsing in deionised water, draining and stoving at 160°C for 1 minute.

The panels pretreated in this way were coated with a Beckers 5 Epoxy stoving primer. The primer was applied using a 25 µm bar coater, stoved at 250°C for 2 minutes 10 seconds (PMT 214-224°C), and given a cold water quench.

The adhesion results are shown in Table 2 below.

Table 2 - Adhesion Testing of Pretreated Panels

	Cross Cut		Falling Impact ^(a)	Cupping Test (6mm) ^(a)	Bend Test (3T) ^(a)
	dry	wet			
1% on Zalutite	0	0	0	30	40
1% on HDG	0	0	0	40	60
1% on Galfan	0	0	0	50	50
10% on Zalutite	0	1	0	70	0
10% on HDG	0	1	0	40	0
10% on Galfan	0	0	0	10	0
HDG control ^(b)	0	1	35	N/A	100

legend:- (a)% coating removed; (b) unpretreated HDG

Example 3 - Adhesion Performance and Corrosion Resistance of Surfaces Treated with the Composition of the Present Invention and Further Coatings

5

A polymer containing 30mol% VPA and 70 mol% AA was applied to HDG (ex British Steel) at three concentrations using the following method.

10

The panels were cleaned in Ridoline 1089 (15 g l⁻¹) at 60°C for 15 seconds, rinsed in mains water, rinsed in deionised water and dried.

15

The polymer solutions were applied at 0.1%w/w, 0.25%w/w and 0.5%w/w in deionised water by immersing the panels in the test solution for 30 seconds at 40°C, spin drying on a sheen spinner for 20 seconds and stoving at 100°C for 5 minutes.

The panels pretreated in this way were coated with a primer and topcoat as follows;

20

primer - a Beckers epoxy primer containing no anti corrosive pigment was applied with a bar coater to give a DFT (Dry Film Thickness) of 8μm and stoved to a PMT of 220°C.

25

topcoat - a commercial coil-coating polyester was applied using a bar coater to give a DFT of 20μm and stoved to a PMT of 232°C.

The adhesion and corrosion results are shown in Table 3 below.

Table 3 - Adhesion and Corrosion Testing of Pretreated Panels

5

Concentration (% w/w)	768 h NSS		Adhesion	
	corrosion spread from scribe/mm	blistering on face	Cupping Test (7mm)/mm removal	Reverse Impact/% removed
Blank ^(a)	17	B4	6	100
0.5	8	B2-3	3	80
0.25	10	B3	1	0
0.1	11	B3	1	0

legend: (a) = Blank, unpretreated HDG

Example 4 - Adhesion Performance and Corrosion Resistance of
10 Surfaces Treated with the Composition of the Present Invention and
Further Coatings.

A homopolymer of vinyl phosphonic acid was applied to HDG (ex
British Steel) at three concentrations using the following method.

15

The panels were cleaned in Ridoline 1089 (15 g l⁻¹) at 60°C for 20
seconds, rinsed in mains water, rinsed in deionised water and dried.

The polymer solutions were applied at 0.1% w/w, 0.5% w/w and
20 1.0% w/w in deionised water by flooding the surface with solution and

spinning off the excess on a sheen spinner for 20 seconds and drying to a peak metal temperature of 80°C.

The panels pretreated in this way were coated with a primer and 5 topcoat as follows:

primer - a Beckers epoxy primer (KE214) was applied using a bar coater to give a DFT of 8 µm and stoved to a PMT of 214°C.

10 topcoat - A PVDF topcoat was applied using a bar coater to a DFT of 25-30 µm and stoved to a PMT of 230°C

The adhesion and corrosion results are shown in table 4 below.

15 **Table 4 - Adhesion and Corrosion Testing of Pretreated Panels**

Pretreatment	Adhesion ^(a)				Corrosion NSS (1000h)	
	Cross hatch		reverse impact	cupping (6mm)		
	dry	wet				
0.1% DIP	0	0	0	0	B1(SL),B4(CE)	
0.5% DIP	0	0	0	0	B1(SL),B4(CE)	
1.0%/DIP	0	0	0	0	B1(SL),B5(CE)	
Accomet C	0	0	0	0	B0(SL),B5(CE)	
untreated	0	0	0	0	B4(SL),B5+(CE)	

legend: (a)adhesion as percent coating removed; Accomet C (Registered Trade Mark), A&W chrome based pretreatment; SL, scribe line; CE, cut edge; DIP, dry in place

Example 5 - Corrosion Performance of Surface Treated with Composition of the Present Invention and Further Coatings.

5 A polymer containing 30 mol% VPA and 70 mol% AA has been applied to 2 panels of different metals at two concentrations using the following method.

10 The panels were cleaned in Ridoline 1089 (15 g l⁻¹) at 60°C for 15 seconds, rinsed in mains water, deionised water and dried.

15 The polymer solutions were applied at 1%w/w and 5%w/w in deionised water on a sheen spinner for 20 seconds and stoved at 160°C for 1 minute.

20 The panels pretreated in this way were coated with a primer and a topcoat as follows;

primer - a Beckers Epoxy stoving primer was applied with a 24 µm bar coater, stoved at 250°C for 2 minutes 10 seconds (PMT 214-224°C) and given a cold water quench;

topcoat - a PVDF (Polyvinylidene di-fluoride) topcoat was applied using a 75 µm bar coater, stoved at 250°C for 2 minutes 30 seconds (PMT 230°C) and given a cold water quench.

25 The panels were diagonally scribed and one edge remove to expose metal substrate. The average DFT was in the range 18.3-26.5 µm. The corrosion results are shown in Table 5 below.

Table 5 - Neutral Salt Spray Testing of Pretreated Panels

	100 h		150 h		360 h		500 h		511 h	
1% on Zalutite	B1	SL	B1-2	SL	B2-3	SL	N/A	N/A	B3	SL
	B4	CE	B4-5	CE	B5*	CE	N/A	N/A	B5*	CE
1% on HDG	B0		B2	SL	B3	SL	N/A	N/A	B5	SL
			B3	CE	B4-5	CE	N/A	N/A	B5	CE
			B1-2		F		N/A	N/A	B2	F
5% on Zalutite	B1	SL	B1-2	SL	B2	SL	N/A	N/A	B3	SL
	B4	CE	B5	CE	B5*	CE	N/A	N/A	B5*	CE
5% on HDG	B0		B2	SL	B3	SL	N/A	N/A	B5	SL
			B2-3	CE	B4-5	CE	N/A	N/A	B5	CE
Accomet C	N/A	N/A	N/A	N/A	N/A	N/A	B5	SL	N/A	N/A
	N/A	N/A	N/A	N/A	N/A	N/A	B5	CE	N/A	N/A
Albritect AZS	N/A	N/A	N/A	N/A	N/A	N/A	B5	SL	N/A	N/A
	N/A	N/A	N/A	N/A	N/A	N/A	B4-5	CE	N/A	N/A
No pretreatment	N/A	N/A	N/A	N/A	N/A	N/A	B5*	SL	N/A	N/A
	N/A	N/A	N/A	N/A	N/A	N/A	B5*	CE	N/A	N/A

5 Legend: SL, scribe line; CE, cut edge; F, Face/field; N/A, not available; AccometC (Registered Trade Mark), A & W chrome based pretreatment; Albritect AZS (Registered Trade Mark), A & W chrome free pretreatment.

CLAIMS

1. A composition adapted to treat the surface of more than one type of metal, the composition comprising at least one organo phosphonate or 5 organo phosphonate species.
2. A composition of Claim 1 wherein the phosphonate species is a mono- or di-phosphonic acid, ester or salt.
- 10 3. A composition of Claim 1 or Claim 2 wherein the phosphonate species is a mono- or di-phosphonic acid, ester or salt containing one or more carbon-to-carbon bonds.
- 15 4. A composition of Claim 3 wherein the phosphonic acid is an alkyl, aryl or alkenyl phosphonic acid.
- 20 5. A composition of Claim 4 wherein the phosphonic acid is octyl phosphonic acid, phosphonosuccinic acid, phosphonopropionic acid, vinylphosphonic acid (VPA), vinylidene-1, 1-diphosphonic acid (VDPA) or phenyl VPA.
- 25 6. A composition of Claim 1 wherein the organo phosphonate or organo phosphonate species is a polymer.
- 30 7. A composition of Claim 6 wherein the polymer is a polymer with pendant phosphonic or di-phosphonic acid groups.
8. A composition of Claim 6 or Claim 7 wherein the polymer is a homopolymer of a phosphonic acid or a salt or an ester of a phosphonic acid.

9. A composition of Claim 7 wherein the polymer is a copolymer of a phosphonic acid or a salt or an ester of said acid together with a second co-monomer.

5

10. A composition of Claim 9 wherein the second co-monomer is an unsaturated carboxylic acid.

11. A composition of Claim 10 wherein the unsaturated carboxylic acid 10 is acrylic acid, maleic acid or methacrylic acid or salts or esters of any of the said acids.

12. A composition of Claim 9 wherein the second co-monomer is an unsaturated sulphonic acid.

15

13. A composition of Claim 12 wherein the unsaturated sulphonic acid is vinylsulphonic acid (VSA), or acrylamido methyl propane sulphonic acid (AMPS) or an ester or a salt of any of the said acids.

20 14. A composition of any one of Claims 7-13 wherein the phosphonic acid is vinylphosphonic acid (VPA), vinylidene-1, 1-diphosphonic acid or phenyl VPA.

15. A composition of Claim 6 wherein the polymer is a terpolymer of 25 an unsaturated phosphonate species and other suitable comonomers.

16. A composition of Claim 15 wherein the other suitable comonomers are unsaturated sulphonic acid, unsaturated carboxylic acid or acrylamide.

17. A composition of Claim 6 wherein the polymer includes a polyester container pendent phosphonic acid groups.

18. A composition of Claim 6 wherein the polymer is a copolymer of 5 vinyl phosphonic acid (VPA) with acrylic acid (AA) wherein the ratio of the components is between 1:99 and 99:1 (VPA:AA).

19. A composition of Claim 18 wherein the ratio is between 2:98 and 30:70 (VPA:AA).

10

20. A composition of any preceding claim wherein the metal surface is cold rolled steel, electro galvanised steel, hot dip galvanised steel and related alloyed alternatives, stainless steel, tin plate or lead coated steel.

15 21. A composition adapted to treat the surface of more than one type of metal substantially as described herein.

20 22. A process for treating a metal surface, the process including the steps of contacting said surface with a controlled amount of a composition of Claim 1 dissolved in a solvent and removing the solvent.

23. A process of Claim 22 wherein the amount of composition to be applied to the metal surface is controlled by dilution of the composition and adjustment of the wet film thickness.

25

24. A process according to Claim 23 wherein the amount of composition residue left on the surface after drying is in the range 0.001g/m² to 10.000g/m².

25. A process according to claim 23 wherein the amount of residue left in the surface after drying is in the range 0.01-1.00g/m².

26. A process of Claim 23, Claim 24 or Claim 25 wherein the
5 composition is applied to the metal surface by flood-spraying or
immersion, and the composition is metered to the required thickness on
the metal surface.

27. A process of Claim 23, Claim 24 or Claim 25 wherein the
10 composition is applied by roller-coating onto the metal surface.

28. A process of Claim 22 wherein the amount of composition to be
applied to the metal surface is controlled by a reaction occurring between
the metal surface and one or more components of the composition.

15

29. A process of Claim 28 wherein the surface is immersed in the
composition for 0.5 seconds to five minutes and at a temperature of 5-
100°C.

20 30. A process of Claim 28 or 29 wherein the metal surface is wiped or
rinsed after contact with the composition.

31. A process of any one of Claims 22-30 wherein the composition is
applied as an aqueous solution.

25

32. A process of any one of Claims 22 to 31 wherein after application
to the metal surface, the composition is allowed to dry passively at
ambient temperature to remove the solvent.

33. A process of any one of Claims 22 to 31 wherein after application to the metal surface the composition is dried positively, to remove the solvent, at a temperature of 60-200°C for 0.1-10 minutes.

5 34. A process of Claim 33 wherein the composition is dried positively at 80-180°C for 0.1-5 minutes.

35. A process of Claim 33 wherein the composition is dried positively at 140-180°C for 0.5-2 minutes.

10 36. A process according to any one of Claims 22 to 35 wherein the metal surface to which the composition is to be applied is cleaned.

15 37. A process according to any one of claims 22 to 36 substantially as described herein.



Application No: GB 9826851.9
Claims searched: 1-37

Examiner: Richard Kennell
Date of search: 2 March 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.Q): B2E (EACA, EACB, EAH, EAK, EAM, EANA, EANC, EKB)

Int Cl (Ed.6): (Not searched)

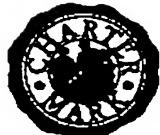
Other: Online (WPI); Selected UK specifications

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
P,X	GB 2322627 A (ALBRIGHT & WILSON), 2 September 1998, whole document	1-14/20-22/30-31 at least
X	GB 2309972 A (CIBA SPECIALITY CHEMICALS), whole document	1-3/20-22/31-32 at least
X	GB 2121419 A (INTERNATIONAL PAINT), whole document	1-3/6-7/20-22/32 at least
X	GB 1489241 A (DYNAMIT NOBEL), whole document	1-4/21-22/26/36 at least
X	GB 1261554 A (MONSANTO), whole document	1-4 at least
P,X	EP 0846733 A (DAIMLER-BENZ), 10 June 1998, whole document	1/6-9 at least
X	EP 0780406 A (ALBRIGHT & WILSON), whole document	1/6-16/18/20-21 at least

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
& Member of the same patent family

A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.
E Patent document published on or after, but with priority date earlier than, the filing date of this application.



The
Patent
Office
22



Application No: GB 9826851.9
Claims searched: 1-37

Examiner: Richard Kennell
Date of search: 2 March 1999

Category	Identity of document and relevant passage	Relevant to claims
X	WO 92/12806 A (HENKEL), see page 7 line 2 - page 8 line 25 and Examples	1- 4/22/26/29 /31 at least
X	US 4978399 A (KODAMA), see phosphonate group in polymer J	1/6-7/20- 22/26/31/ 36 at least

X Document indicating lack of novelty or inventive step	A Document indicating technological background and/or state of the art.
Y Document indicating lack of inventive step if combined with one or more other documents of same category.	P Document published on or after the declared priority date but before the filing date of this invention.
& Member of the same patent family	E Patent document published on or after, but with priority date earlier than, the filing date of this application.